ISOTOPIC INVESTIGATION OF AN ARAGONITE MARBLE

ORCAS ISLAND, WASHINGTON

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for the B.Sc. Degree in Geology

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ABSTRACT

The carbonate fraction of an aragonite marble (20% aragonite, 80% calcite) from the Orcas Formation, Washington has an $^{87}Sr/^{86}Sr$ ratio = 0.70779 ± 0.00028. This is concordant with the ratio for Early to Middle Triassic sea water and thus could imply a Triassic age, consistent with fossil evidence.

The $^{87}Sr/^{86}Sr$ ratio for the non-carbonate residue of the sample is 0.7123 ± 0.0007 and indicates that Sr homogenization during mid-Cretaceous metamorphism ($250^{o}C$, 2.5 kB) may not have occurred, allowing the calculation of a Devonian age for the clay fraction

The strontium concentration of the carbonate (614 ppm) is consistent with the conclusion by Vance, (1975) that the aragonite is a recrystallized metastable product of original calcite.

A $\delta^{18}O$ value of $+18.9^{o}/oo$ and $\delta^{13}C$ value of $+3.1^{o}/oo$ for the carbonate fraction is consistent with a known marine origin for the rock.

A $\delta^{13}C$ value of -26.1‰ for amorphous carbon of the residue fraction indicates a photosynthetic origin.

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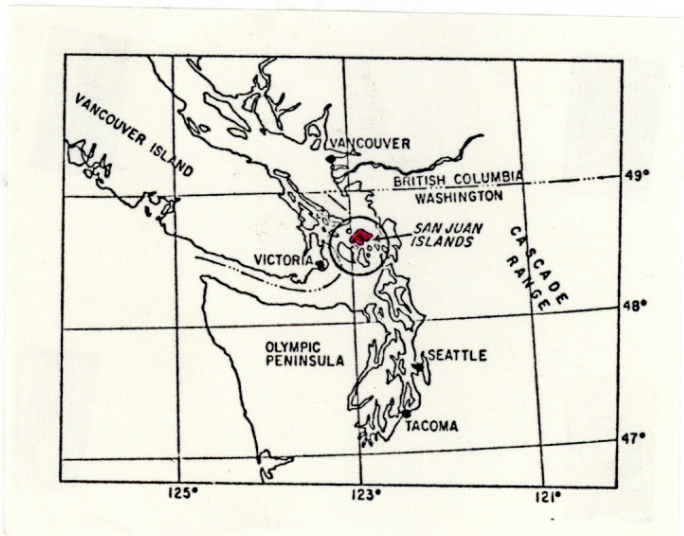
INTRODUCTION

The main purpose of this investigation is to date a sample of aragonite-marble from the Orcas Formation at the McGraw-Kittinger quarry, Orcas Island Washington, (refer to Map 1) by using the $^{87}Sr/^{86}Sr$ ratio of the carbonate phase in conjunction with data reported by Peterman et al. (1971). The carbonate sample used in this investigation contains no fossils and therefore, the Common Strontium method is the only method that can be employed.

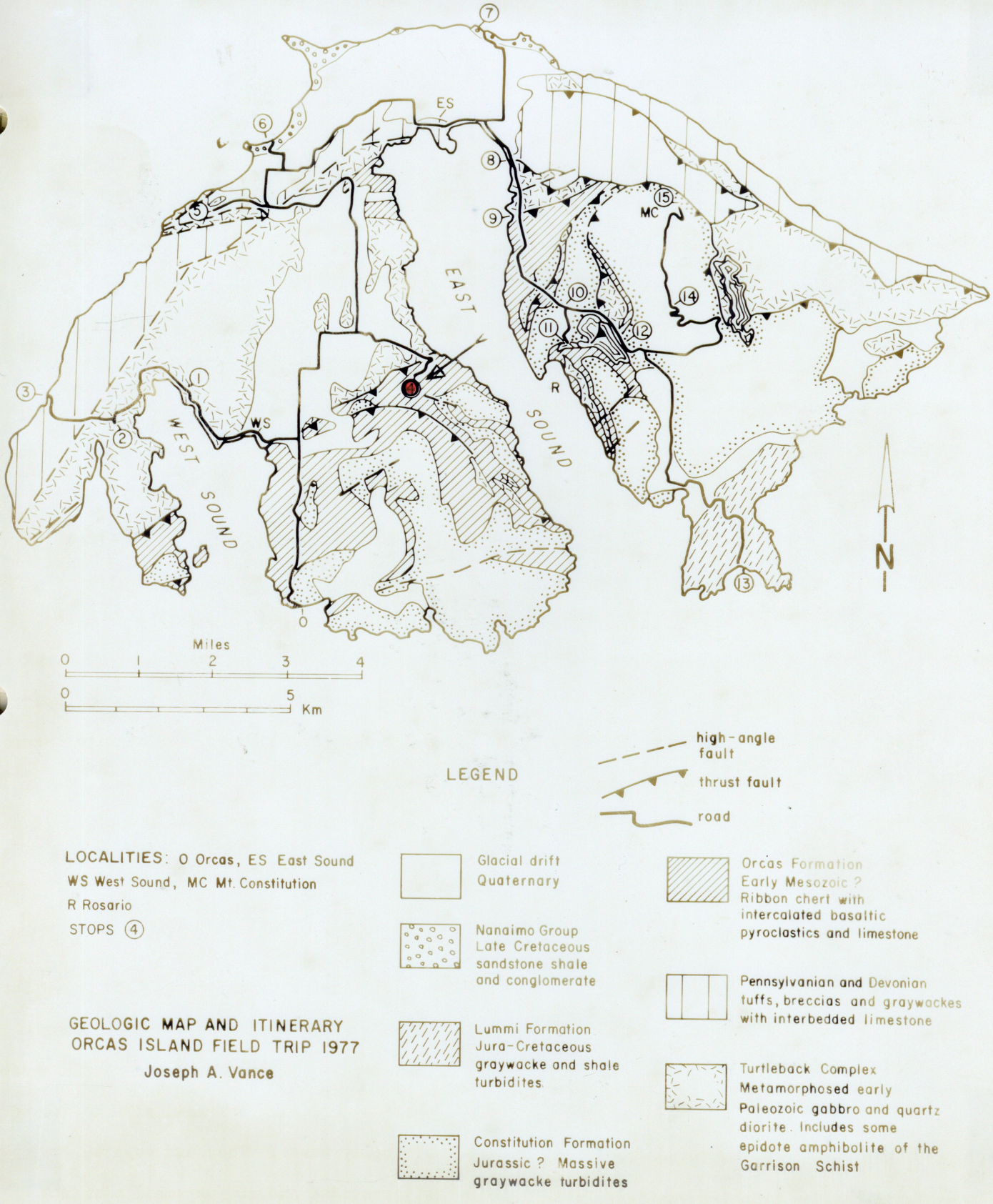
Orcas Island, Washington is one of the San Juan Islands which are located east of Vancouver Island and north of the Olympic Peninsula in the vicinity of the North Cascade Range (refer to Map 2).



Map 2.

(Map showing the San Juan Islands and vicinity. Orcas Island is delineated in red).

The Orcas Formation consists primarily of grey ribbon cherts, locally as thick as 500 meters (Vance, 1971). Submarine basaltic volcanic rocks make up approximately 20% of the Orcas Formation (Vance, 1971). Aragonite marble



Map 2.
Orcas Island, Washington

(The McGraw-Kittinger is shown with an arrow and red dot.)

occurs in limestone lenses up to 20 meters in thickness, which are distributed throughout the Orcas Formation (Vance, 1971).

The rocks of the Orcas Formation are part of a large structural unit that experienced mid-Cretaceous metamorphic conditions intermediate between prehnite-pumpellyite and lawsonite-albite facies (Vance, 1971). This is evidenced by the presence of both prehnite and lawsonite in rocks directly overlying the Orcas Formation, and the "transformation" of large limestone bodies of the Orcas Formation to aragonite marble (Vance, 1971). "The structure and metamorphism of these rocks are consistent with tectonic burial related to subduction at a convergent plate margin" (Vance, 1971).

Most fossil evidence supports a Mesozoic age for the Orcas formation (see Appendix). Rocks of other ages are found, the oldest being Devonian in age (Whetton et al, 1978). These rocks may be exotic, having been technically emplaced during transport (Vance, 1971). The writer knows of no previous age determination for limestones at the McGraw-Kittinger quarry on Orcas Island and therefore, this work contributes to a growing volume of age determinations for rocks of the Orcas.

Also, results obtained from the following analyses are reported and implications given:

1. X-ray diffraction
2. X-ray fluorescence (Strontium and Rubidium
3. Thin section study
4. Oxygen and carbon isotope analyses made on the carbonate fraction of the sample
5. Strontium, carbon and sulfur analyses made on the acid insoluble fraction of the sample

THE $^{87}Sr/^{86}Sr$ RATIO OF MARINE CARBONATE ROCKS

In 1948 Wickman proposed that $^{87}Sr/^{86}Sr$ ratios of marine carbonates might be used in determining the age of precipitation. This led to the accumulation of a large volume of information concerning strontium in the world's oceans and changes in the $^{87}Sr/^{86}Sr$ ratio during geologic time.

Strontium has a mean residence time in the oceans of approximately 10^6 years (Brass, 1975). This is considered relatively long compared to the time required for the isotopic mixing of strontium isotopes and consequently sea-water everywhere in the world's oceans contains strontium whose $^{87}Sr/^{86}Sr$ ratio is 0.7091 (Faure and Powell, 1972). Isotopic homogeneity was demonstrated by Faure et al. (1965), who analyzed water samples from the eastern side of the Hudson Bay and obtained an $^{87}Sr/^{86}Sr$ ratio of 0.7093 ± 0.0003, identical, within analytical uncertainty, to the ratio for ocean water. Evidently, despite the flux of radiogenic strontium entering the Hudson Bay ($^{87}Sr/^{86}Sr = 0.721$ for entering riverwater), and despite the fact that only a narrow inlet connects the Hudson Bay to the North Atlantic Ocean, strontium in the Hudson Bay possesses a "marine" $^{87}Sr/^{86}Sr$ ratio. This is due to the high concentration of strontium in sea water relative to the strontium concentration in river water entering the bay (Faure et al., 1965).

Present evidence suggests that strontium in sea water at any instant of time in the past also had a uniform isotopic composition. Peterman (1970) verified this for Cretaceous epicontinental seas surrounding North America. No contrary evidence for other times in the geologic past exists.

Wickman (1948), Gast (1955), Hedge and Walthall (1963), and Hurley (1965) advocated a monotonically time dependent increase of the ocean's $^{87}Sr/^{86}Sr$ ratio since Precambrian. Peterman et al. (1970) analyzed unreplaced epicontinental shell carbonate from mollusks of various ages. Their data indicate that the ratio did not increase monotonically but varied in an orderly fashion between limits of 0.7091 and 0.70675 since mid-Devonian time (see Fig. A).

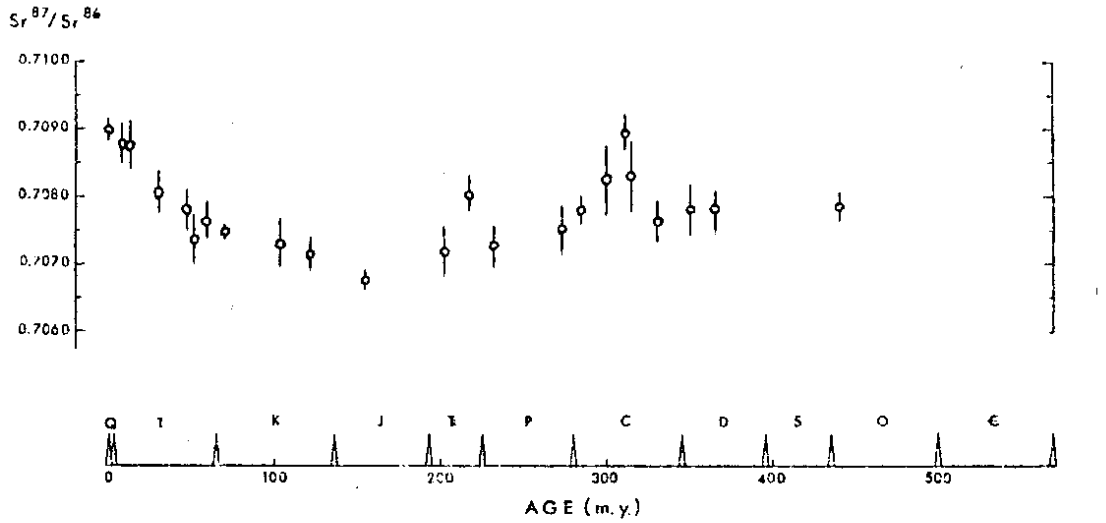


Fig. 2. Variation in Sr^{87}/Sr^{86} values for sea water during most of Phanerozoic time. The vertical bars represent the 95 per cent confidence level about the mean points.

FIG A Peterman et al. (1970, p. 111)

This conclusion is based on the premise that unreplaced carbonate minerals possess an $^{87}Sr/^{86}Sr$ ratio identical to the $^{87}Sr/^{86}Sr$ of the sea water in which it precipitated since neither natural or biogenic fractionation of strontium isotopes has been observed in nature. The concordance between the modern ocean value and recently precipitated marine carbonate phases has been shown by Hedge and Walthall (1963), Faure et al. (1965), Peterman et al. (1970), Dasch and Biscaye (1971). Therefore the $^{87}Sr/^{86}Sr$ ratios of unaltered shell carbonate and limestone of different ages are direct indicators

of the $^{87}Sr/^{86}Sr$ ratios for seawater during geologic time.

Peterman's results have been verified by other investigators (Dasch and Biscaye (1971), Veizer and Compston (1974), Tremba et al. (1975), Faure et al. (1978)), and the variations shown on Fig. *A* are widely accepted (Faure, 1978).

Faure et al. (1965) proposed that the present-day $^{87}Sr/^{86}Sr$ ratio for seawater could be described as a mixture of three isotopic varieties of strontium contributed to the oceans through the chemical weathering of three rock types:

1. Old continental sialic rocks having an $^{87}Sr/^{86}Sr$ ratio of about 0.720 ± 0.005.
2. Phanerozoic marine carbonate rocks with an $^{87}Sr/^{86}Sr$ ratio of 0.708 ± 0.001.
3. Young volcanic rocks whose $^{87}Sr/^{86}Sr$ ratio is 0.704 ± 0.002.

Changes in the $^{87}Sr/^{86}Sr$ ratio of the oceans during the geologic past reflect changes in the relative proportions of these isotopic varieties that were being contributed to the oceans by chemical weathering of continental and marine rocks (Faure, 1978).

DATING OF MARINE CARBONATE ROCKS

A marine carbonate rock containing no fossils may be datable by the "Common Sr Method" even when information concerning the sample's stratigraphic and structural position is not available. Measurement of the $^{87}Sr/^{86}Sr$ ratio is the only possible dating technique employable in such cases. The method is limited because Peterman's graph shows that the $^{87}Sr/^{86}Sr$ ratio is not a unique function of age. The investigator obtains several dates corresponding to times in the past when sea water had an $^{87}Sr/^{86}Sr$ ratio concordant with that measured for the carbonate.

Stratigraphic and structural information may disqualify some of the possible dates. If geologic relations suggest that a certain marine carbonate rock is Mesozoic in age, the $^{87}Sr/^{86}Sr$ will indicate two possible dates. The method is most effective when relations suggest a post-middle Jurassic age. In this interval Peterman's graph is monotonic increasing.

In cases where the age is controversial, i.e., available data suggest an "either or" age, it is possible that the $^{87}Sr/^{86}Sr$ ratio may be used as a discriminating factor. Tertiary marine carbonates can be distinguished from Cretaceous marine carbonates, Jurassic from Triassic, Triassic from Permian.

When micro or macro fossil data are available, one of the possible dates indicated by the ratio should be compatible with the age shown by the fossils. This is true provided that the $^{87}Sr/^{86}Sr$ ratio was not changed subsequent to deposition. If discordance is observed, paleontological evidence takes priority.

The criteria that must be met by a carbonate sample for the application

of the dating method include:

1. The sample is marine in origin and Devonian or younger in age.
2. The $^{87}Sr/^{86}Sr$ ratio has not significantly changed subsequent to deposition.

The latter can result from strontium isotope exchange between the carbonate and detrital fractions of the rock during burial, diagenesis, metamorphism, or during the analysis. The chemical weathering of aluminum silicates leads to the formation of clay minerals having $^{87}Sr/^{86}Sr$ ratios not markedly different from their parent rocks (Dasch, 1969). Although sea water-clay mineral strontium isotope exchange reactions are recognized (South Pacific Ocean smectite studies, Clauer, 1978), equilibration of Sr isotopes during transport and deposition in a marine environment generally does not occur (Dasch, 1969).

Open system behavior with respect to strontium subsequent to the carbonate formation can also change the primary ratio. Present evidence indicates that limestones are open system donors of strontium; the loss is dependent on the number of times the limestone has been recrystallized (Shirmohammadi and Shearman, 1966). Kinsman (1969) has shown that the primary strontium concentration in carbonate rocks depends mainly on the $\frac{M{+}{+}Sr}{M{+}{+}Ca}$ ratio and temperature of the precipitating solution. (The relation is held most closely for dilute solutions). If the $^{Sr}/Ca$ ratio in the oceans has not changed significantly since Paleozoic time (Lowenstam, 1961; Turekain 1964, Kinsman's data indicate primary strontium concentrations of 7000-10,000 ppm and 1200-2000 ppm for marine aragonites and calcites respectively. (Substitution of Sr for Ca in the orthorhombic aragonite structure is greater than that for Ca in the hexagonal calcite structure.) However, subsequent dissolution and reprecipitation during diagenesis or metamorphism can lead to substantial decreases in the concentrations, commonly 600-800 ppm for calcites, 2000-6000 ppm for aragonites. The magnitude of the loss during a diagenetic event depends

generally on the volume and Sr^{++}/Ca^{++} ratio of the participating pore fluid (Kinsman, 1969). Concurrent changes in the primary carbonate's $^{87}Sr/^{86}Sr$ ratio could occur when participating pore fluids contain dissolved strontium having an $^{87}Sr/^{86}Sr$ ratio much different.

Recrystallization in sea water early in the history of a carbonate probably would not alter the primary ratio significantly. Continental waters have variable $^{87}Sr/^{86}Sr$ ratios, often highly radiogenic and when acting as the participating pore fluid, could change the primary ratio. Appreciable interaction with continental waters might perhaps be indicated by other isotopic data, such as the $\delta^{18}O$ and $\delta^{13}C$ values for the carbonate.

ANALYTIC METHODS

Approximately two Kg of the whole rock sample were ground to about 60 mesh using a rock crusher and pulverizer. In order to avoid contamination, parts of the apparatus that come in contact with a sample were thoroughly cleaned before use. The weight percentage of non-carbonate residue in the whole rock sample was determined as follows:

A portion of the powder was weighed on an analytical balance and then added to a clean beaker containing cold 2.25 N HCl prepared by dilution of 12 N reagent grade HCl with double distilled and demineralized water. After dissolving the carbonate minerals, the insoluble residue was washed twice in double distilled-demineralized water and then dried in an oven at 100°C overnight. The residue was weighed and the abundance of non-carbonate residue was found to be 0.42%. An X-ray diffraction scan of the residue verified that no carbonate phases were present. This might be an over-estimation of the value due to moisture adsorbed onto clay surfaces after the residue was taken out of the oven.

Preparation of Pellets

A pellet of whole-rock powder and pellet of non-carbonate residue was prepared for X-ray diffraction and X-ray spectrometry. X-ray diffraction was used in determining the mineral compositions of the whole rock sample and non-carbonate fraction of the sample. X-ray spectrometry was the method used in determining the Sr and Rb concentrations in the whole rock sample and non-carbonate fraction of the sample. Non-carbonate residue was obtained using the procedure outlined above. Residue and whole rock powder were made to pass a 200 mesh screen. 2.6 grams of sample material were packed in a 1.25 in. diameter jacket of 6.6 grams of Boric acid under a pressure of 12 tons per sq. in. for two minutes.

X-RAY DIFFRACTION

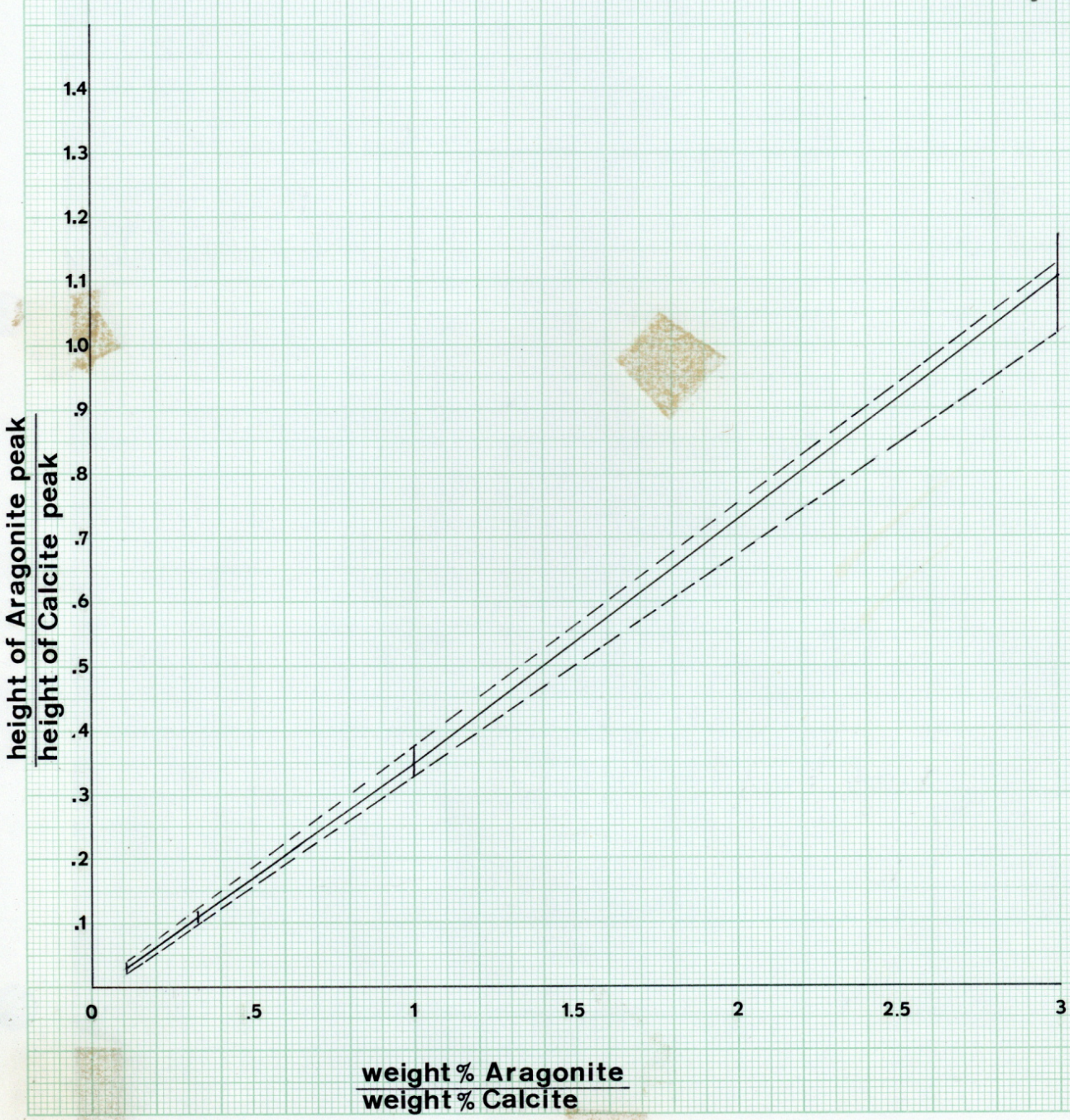
Pellets were analyzed with a Diano Corp. Model XRD-6 X-ray diffractometer utilizing Nickel filtered CuKα radiation. Machine settings were 45 kVP and 15 ma. Incident and diffracted X-rays were collimated with a 1^{o} beam slit and intensities were measured with a scintillation counter driven at a rate of $2^{o}2\theta$ per minute. Peaks were recorded on a strip chart. Mineral identifications were determined by the detection of 2 peaks per mineral at 2θ values given by Chao (1969).

Carbonate Minerals

A 2^{o}-55^{o} diffraction scan of the whole rock pellet attested to the whole rock's homogeneity showing peaks corresponding only to calcite and aragonite. The weight percentage of aragonite was determined as follows. Four laboratory standards were prepared by Faure in calcite/aragonite weight proportions of $^{90}/10$, $^{75}/25$, $^{50}/50$ and $^{25}/75$. The standards were scanned four times each between 2θ values of 25^{o} and 30^{o}. The absolute height intensities of the principal calcite and aragonite peaks at 29.43^{o} and 26.24^{o} respectively, were measured. The average (aragonite intensity/calcite intensity) ratio for each standard was plotted vs. its corresponding aragonite/calcite weight proportion (see Figure 1). Vertical bars include the range of values obtained in the four analyses of the standards. Solid line segments are located through the means.

Six scans of the whole rock pellet of this study yielded an average (aragonite int./calcite int.) ratio of 0.82 ± 0.009. This corresponds to an aragonite weight percentage of about 18-22%.

FIGURE I



Non-Carbonate Minerals

The principal mineral components of the non-carbonate fraction of the whole rock as shown by a 2^{o}-60^{o} scan of the non-carbonate pellet are quartz-(10% of non-carbonate), pyrite - (2% of non-carbonate) and a regularly mixed double layered clay mineral. The principal peaks of serpentine and anatase were also detected at very low intensities. No illite is present.

The following evidence suggests that the mixed clay mineral consists of regularly alternating layers of smectite ($d_{001} = 15\text{Å}$) and a non-expandible clay mineral, probably chlorite ($d_{001} = 14\text{Å}$). The X-ray scan displayed an integral set of basal reflections for a clay mineral with a (001) d-spacing of 28.6Å. After a 12 hour, 25^{o}C treatment with methylene glycol the (001)d - spacing swelled to 31.6Å. When the sample was heated in an oven at 300^{o}C for one hour, the (001) d spacing collapsed to about 27.6Å.

The identical treatment of a clay mineral where smectite and chlorite layers alternate regularly leads to the following observations:

1. An integral set of basal reflections corresponding to a $d_{001} = 15\text{Å}$ (smectite) + 14Å (chlorite) = 29Å.
2. After treatment with methylene glycol, $d_{001} = d_{001}$ (glycolated chlorite) + d_{001} (glycolated smectite) = 17.5Å + 14Å = 31.5Å. Smectites expand along their c-axes to about 17-18Å (Carrol 1970); chlorite does not respond to this treatment.
3. After heating at 300^{o}C for 1 hour, $d_{001} = d_{001}$ (heat treated smectite) + d_{001} (heat treated chlorite) = 10Å + 14Å = 24Å. The interwater layer of montmorillonite is driven off resulting in a contraction to $d_{001} = 10\text{Å}$; however, the presence of cations attached to surfaces of the interwater cavity can prevent the complete contraction. Chlorite

does not possess an interwater layer; d_{001} is unaffected (Carrol, 1970).

An estimate of the weight % of quartz in the non-carbonate fraction was calculated from the following calibration equation (after Boger, 1971).

$$\text{quartz weight \%} = \frac{\text{P.H.}}{\text{Mo K}\alpha\ \text{(Compton)}} \times .01639 \times 10^5$$

where:

P.H. is the peak height intensity measured on the 1000 scale of the 26.66° 2 quartz peak.

$Mo_k\alpha$ (Compton) is obtained with an X-ray spectrometer and is the intensity of the Compton scattered portion of the $Mo_k\alpha$ peak measured as the number of counts accumulated in 100 seconds. This parameter corrects for matrix effects and will be explained later.

An independent check was made using a calibration equation after Nardone (1977). The quartz peak height at 20.85° 2θ is measured in counts/second.

$$\text{quartz weight \%} = \frac{\text{P.H.}}{\text{Mo K}\alpha\ \text{(Compton)}} \times .71 \times 10^{-4} + 2.58$$

Data for the Orcas non-carbonate sample is reported in Table 1.

TABLE 1 - Data used to calculate the weight percentage of quartz in the non-carbonate fraction.

$Mo_{k\alpha}$ (Compton) counts accumulated in 100 sec.	P.H. counts/sec	SiO_2 Weight %
33637	(26.66°) = 200	9.5
33998		
34851	(20.85°) = 40	10.8
34692		
34791		Mean: 10%
35193		
Mean: 34557		

The quartz weight percentages calculated from the Z calibrations (9.5% and 10.8%) are in satisfactory agreement.

STUDY OF THE NON-CARBONATE FRACTION

Non-carbonate powder was viewed under a binocular scope at a magnification of 10 power. Quartz grains are very fine silt sized and rounded. All the pyrite crystals are cubic, euhedral, and in the fine silt grain size or smaller. Crystal faces are remarkably unaltered and display magnificent striations. The concentration of pyrite is estimated ≤ 2% of the non-carbonate fraction.

Hand Specimen

The non-carbonate phases appear to be concentrated in layered fashion within the whole rock sample. (Only very small quantities of clay or amorphous carbon is required to darken a carbonate). Boundaries are generally diffuse but tight folding and small scale shearing of the layers are clearly visible. Pyrite grains occupy tiny shear fractures (1/80 in. wide) parallel to and within the darker non-carbonate layering.

Thin Section

Two thin sections were prepared from rock slices cut perpendicular to each other and the layering. Features indicating pressure solution of calcite grains (welded grains) at the contacts of residue concentrations are not seen and is an argument against a stylolitic origin of the residue concentrations. Again, shearing parallel to and within residue layering is indicated by the presence of tiny broken calcite grains within shear fractures. Although clay minerals are present within the purer carbonate layers, pyrite does not occur in these areas. Quartz was not detected in thin section.

There are two possible explanations for the distribution of non-carbonate phases in the whole rock, consistent with the observations. These are:

1. Minor sediment (clay + quartz + amorphous carbon) was deposited continuously with the carbonate and thus the original distribution was

homogeneous throughout the rock. The present layering is due to a stylolitic origin; however, evidence for this origin has since been destroyed by recrystallization of the carbonate. Folding of layers could be coeval to or post-date the formation of the layering.

2. Layers of non-carbonate minerals are primary bedding and represent thin sediment (quartz + clay + amorphous carbon) layers that were later tightly folded within the sample.

The association of pyrite with the non-carbonate minerals could suggest a possible diagenetic origin. It is also possible that the pyrite is epigenetic, related to the introduction of fluids along the fractures from an outside source. Advocates of the latter hypothesis could argue that there is nothing unusual about the occurrence of pyrite with thin beds of non-carbonate sediment and its absence from the carbonate layers. Layering can create a structural anisotropy within the rock, along which shearing preferentially occurs and outside of which carbonate layers would flow under pressure. (No shear fractures are seen in the carbonate layers of the sample). Fractures within non-carbonate sediment layers would be the only avenues offered to fluids, the carbonate rock remaining essentially impermeable.

As a purely speculative exercise, it is of interest to consider the origin of the regularly mixed layered smectite-chlorite clay.

Both smectite and chlorite form from an alteration of iron-magnesium silicate minerals, hence basaltic rocks. Although mixed layered smectite-chlorite clays can form as the original weathering products of igneous rocks, Boles and Franks (1978) indicate that such clays can form from the diagenesis of original smectite. They observed changes in the clay mineral composition of the Wilcox shale with depth and attributed them to increasing temperature. Some of the changes they observed and the interpretations they gave

are:

1. The destruction of smectite layers and conversion to illite layers, provided K^+ is present. The conversion temperature is variable and depends on the chemical composition of the smectite.

2. At temperatures greater than 125^{o} chlorite forms at the expense of smectite. Fe and Mg are released during the breakdown of smectite.

3. In general, clay mineral transformations pass through randomly mixed arrangements into orderly mixed arrangements, followed by the eventual destruction of all expandible layers.

Since the metamorphic temperatures in the Orcas Formation reached at least $200^{o}C$, the regularly mixed layered clay of the Orcas sample could have formed from original smectite by the mechanism of Boles and Franks (1978).

DETERMINATION OF Rb and Sr CONCENTRATIONS

A Diano Corp. XRD-6 air path spectrometer with a Mo tube and scintillation detector was used to determine the concentrations of strontium and rubidium in the carbonate and non-carbonate phases of the whole rock. Primary-x-radiation was collimated with a 0.010 in. Soller slit; fluorescent radiation was dispersed with a lithium fluoride crystal cut parallel to the 220 crystallographic plane. The machine was turned on 45 minutes prior to use with settings of 65 kvp and 55 ma.

Relevant radiations were detected at the following goniometer settings:

$Mo_{K\alpha}$ Compton	30.00
B_1	35.2
$Sr_{K\alpha}$	35.85
B_2	36.50
$Rb_{K\alpha}$	37.99
B_3	38.58

B_1, B_2, and B_3 are used to determine background radiation, the intensity of which is subtracted from measured $K\alpha$ x-radiation. Background is assumed to be linear as a function of 2θ .

$$Sr_{K\alpha}\ Int = Int\ (35.85°) - \frac{B_1 + B_2}{2}$$

$$Rb_{K\alpha}\ Int = Int\ (37.99°) - B_3 + \left(\frac{B_2 - B_3}{2.08}\right).59$$

SR CALIBRATION CURVE

For thick specimens, the intensity of the background corrected Sr_k spectral line (λ = .877) is given by

$$\text{Int } Sr_{k\alpha} = \frac{(K)(\text{ppm Sr})}{\mu_{(.877)}}$$

(Reynolds, 1963)

K is a proportionality constant for the particular spectrometer used; ppm Sr is the strontium concentration in the sample; $\mu\lambda$ (.877) is the sample's mass absorption coefficient for Sr_k radiation. Division by $\mu\lambda$ (.877) corrects for the fraction of $Sr_{k\alpha}$ radiation adsorbed and scattered by matrix elements of the sample. (For limitations see Reynolds). Reynolds demonstrated the existence of an inverse relationship between the intensity of the incoherently scattered fraction of primary X-rays (scattered 90° to incident direction) and the mass adsorption coefficient of the sample over a $\mu\lambda$ range common to geologic materials (7.37 - 20.12). Substituting $(Mo_{k\alpha}$ Compton$)^{-1}$ for μ (.877) in the above equation yields

$$\frac{\text{Int } Sr_{K\alpha}}{Mo_{K\alpha}\text{ (Compton)}} \propto \text{ppm Sr}$$

From this relationship, a Sr calibration curve can be constructed, by plotting known Sr concentrations of standards as a function of their measured Int $Sr_{K\alpha}$ values. The curve is then used to determine Sr concentrations

---

$Mo_{k\alpha}$- Compton

in unknowns.

Figure 2 is the Sr calibration curve obtained in this study from the analysis of pellets prepared from U.S. Geological Survey rock standards W-1, G-2, GSP-1, BCR-1 and AGV-1. The standards were run in triplicate between the analysis of an internal monitor (48-R3); the time for the start of each run was recorded. The background corrected Sr_k intensity and background uncorrected $Mo_k\alpha$- Compton intensity obtained in an individual run were used to calculate $SrK\alpha/Mo_k\alpha$ Comp. The values calculated for 48-R3 were plotted vs. the time that the corresponding analysis began. (Fig. 3 - converted to elapsed time). The graph was used to normalize $Sr_{k\alpha}/Mo_k\alpha_{Comp.}$ values for the standards to .3125 for 48-R3 thus minimizing the effect of machine drift.

The mean value for each standard was calculated and plotted vs. its corresponding strontium concentration (Flanagan, 1973). The straight line was fitted by the method of least squares and forced through the origin by weighting the point (0,0) 30 times in the regression equations. The equation of the line obtained is:

$$Sr = 616.02 \left(\frac{Sr_K\alpha \text{ Intensity}}{Mo_K\alpha \text{(Compton) Intensity}} \right) + .29 \text{ ppm}$$

corr. coefficient = .99998

Whole rock and non-carbonate pellets were analyzed using the same procedure used in the analysis of U.S.G.S. standards. Sr concentrations were determined from the above equation. The results are reported in

FIGURE 2

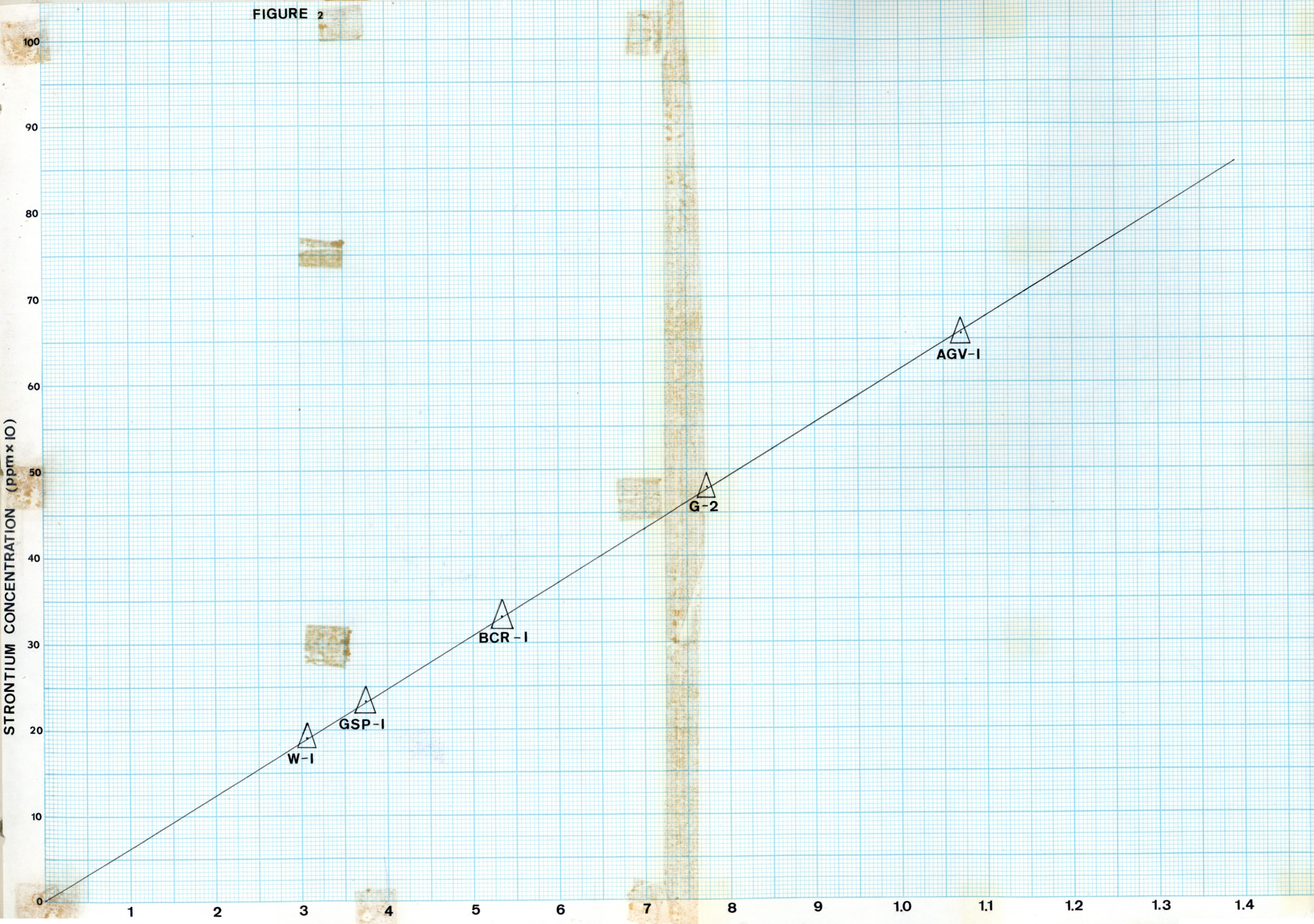

STRONTIUM CONCENTRATION (ppm x 10)
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
1.0
1.1
1.2
1.3
1.4
Sr net / Mo K-alpha Compton
W-1
GSP-1
BCR-1
G-2
AGV-1

FIGURE 3

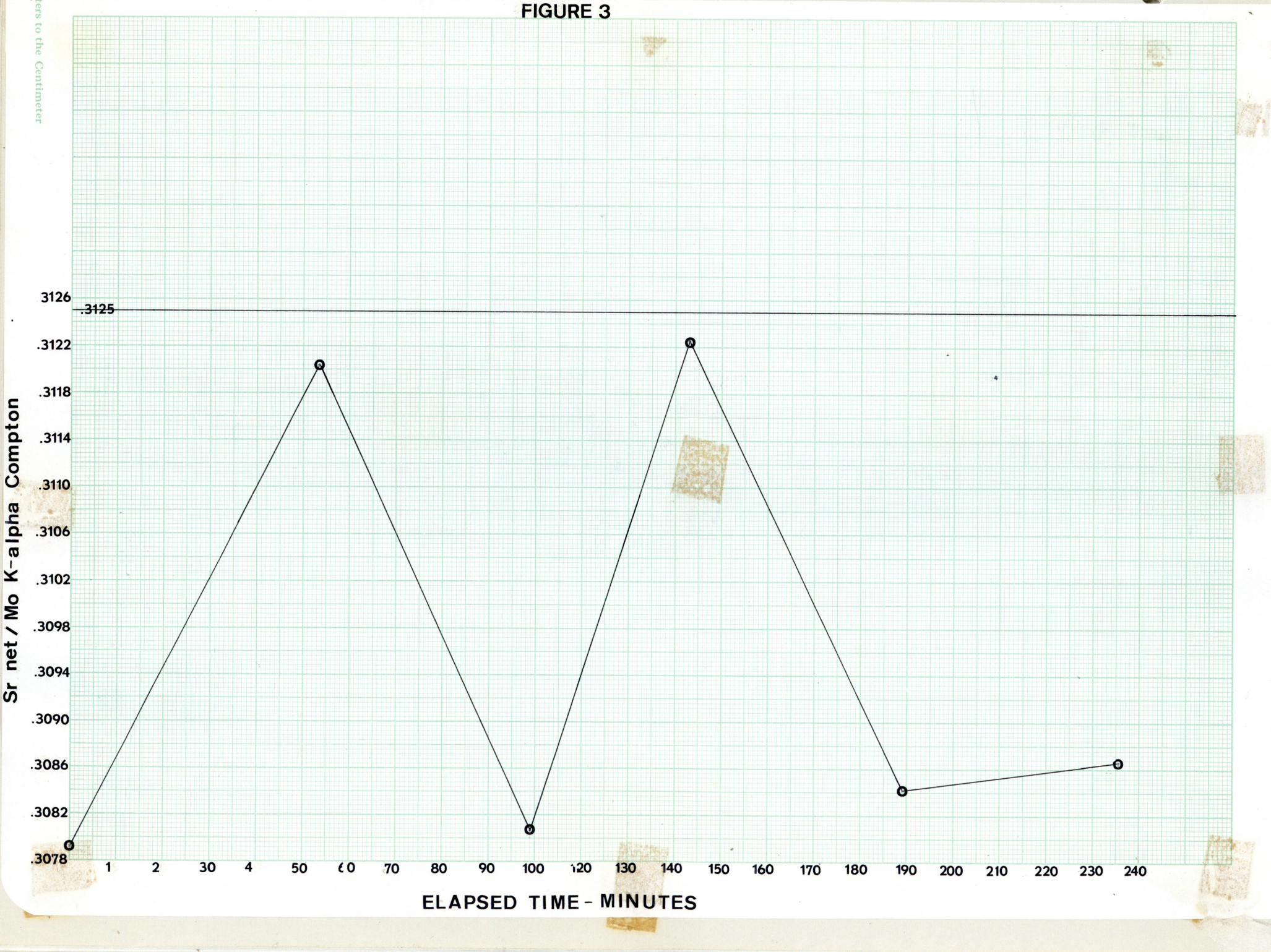

Sr net / Mo K-alpha Compton
3126
.3125
.3122
.3118
.3114
.3110
.3106
.3102
.3098
.3094
.3090
.3086
.3082
.3078
1
2
30
4
50
60
70
80
90
100
120
130
140
150
160
170
180
190
200
210
220
230
240
ELAPSED TIME - MINUTES

Table 2.

TABLE 2. Sr concentrations in whole rock and non-carbonate fraction of Aragonite Marble, Orcas Island, Washington

Sr. conc. whole rock ppm.	Sr. conc. non-carbonate ppm
612 611 Mean = 612 $\pm$ 1 ppm	36 40 39 41 40 41 Mean = 40 $\pm$ 2 ppm

The calculation for the strontium concentration within the carbonate phases (80% calcite, 20% aragonite) is

$$\text{Conc. Sr}_{(\text{carb})} = \frac{\text{Conc. Sr}_{(\text{whole rock})} - \text{weight fraction (non-carb)} \times \text{Conc. Sr (non-carb)}}{\text{weight fraction (carb.)}}$$

$$614.3 = \frac{612 - .004 \times 40}{.996}$$

Rb concentrations were determined from the following calibration equation:

$$\text{Rb} = 814.188 \left(\frac{\text{Rb K}\alpha \text{ Intensity}}{\text{Mo K}\alpha \text{ (Compton) Intensity}} \right) + .015 \text{ ppm}$$

Corr. coefficient = .999797

The results are reported in Table 3.

TABLE 3. Sr concentrations in whole rock and non-carbonate fraction of whole rock, aragonite-marble, Orcas Island, Washington.

Rb. conc. whole rock ppm.	Rb. conc. non-carbonate ppm.
0	13
0	17
0	15
0	18
	16
	12
	Mean = 15 $\pm$ 2 ppm.

Vance (1968) concluded from mineral associations and structural information that the Orcas aragonite is a metastable product of recrystallization at moderate pressure of original calcite. This is compatible with a Sr concentration of 614 ppm, which is inconsistent with an original aragonite formation followed by recrystallization to calcite. This is seen by assuming conservative Sr concentrations for calcite recrystallized from aragonite = (600+ ppm) and aragonite (2000-3000 ppm.). For the Orcas carbonate (20% aragonite, 80% calcite) a Sr concentration of at least 880-1080 ppm. would be expected.

A Sr concentration of 614 ppm, determined for the carbonate sample is obviously lower than 880-1080 ppm and is more consistent with original calcite formation.

CARBON ISOTOPE COMPOSITION

1. Carbonate Minerals

The $^{13}C/^{12}C$ ratio for the carbonate was measured by Geochron Laboratories and reported in standard δ notation relative to the University of Chicago isotope standard (PDB). The reported value is $\delta^{13}C = +3.1^{o}/oo$. Factors controlling the $^{13}C/^{12}C$ ratio and hence the $\delta^{13}C$ value for a carbonate include:

1. The temperature of precipitating solution.
2. The relative proportions of CO_2 contributed to the precipitating solution by oxidation of plant material, the atmosphere and dissolved carbonates (Landergren, 1954).
3. The hydrogen ion activity and other chemical parameters of the precipitating solution which govern activities of $CO_3^{=}$ and HCO_3^{-} (Deuser and Degens, 1967).
4. Fractionation of carbon isotopes between aqueous CO_2 and carbonate species (Deuser and Degens, 1967).
5. The rate of precipitation (McCrea, 1950).

$\delta^{13}C$ Definition (relative to PDB)

$$\delta^{13}C = \frac{^{13}C/^{12}C_{(sample)} - ^{13}C/^{12}C_{(PDB)}}{^{13}C/^{12}C_{(PDB)}} \times 10^{3}\ ‰$$

Experiments by Baertchi (1957) indicate a fractionation factor of 1.010 at 26°C for the reaction $^{13}CO_2(g) + CaC^{12}O_3 \rightleftharpoons C^{12}O_2(g) + CaC^{13}O_3$ resulting in about a 1% enrichment in ^{13}C for carbonate precipitated in isotopic and chemical equilibrium with aqueous CO_2.

The control that CO_2 present in the precipitating solution has on the isotopic composition of carbonates is seen in trends of $\delta^{13}C$ values. Marine carbonates have uniform $\delta^{13}C$ values of about $+.56^{o}/oo$ to $1.55^{o}/oo$ (Keith and Weber, 1964). Fresh water carbonates are variably enriched in ^{12}C relative to marine carbonates and have $\delta^{13}C$ values of about $-4.93^{o}/oo$ $-2.75^{o}/oo$ (Keith and

Weber, 1964). The difference is due to the contribution of CO_2 derived from the oxidation of plant matter (Faure, 1978). $\delta^{13}C$ values for terrestrial plants range from $-24^{o}/oo$ to $-34^{o}/oo$, highly enriched in ^{12}C relative to CO_2 derived from the atmosphere ($\delta^{13}C = -7^{o}/oo$) (Faure, 1978). A $\delta^{13}C$ value of +3.1 for the Orcas carbonate is consistent with a marine origin and indicates that no post depositional interaction with continental waters enriched in ^{12}C has occurred.

2. Amorphous Carbon

The $^{13}C/^{12}C$ ratio for the amorphous carbon fraction of the noncarbonate was measured by Geochron Laboratories and reported in standard δ notation. The reported value is $-26.1^{o}/oo$.

Factors controlling the $\delta^{13}C$ value for organic matter in sediment include:

1. Nature of organic matter, terrestrial plant debris ($\delta^{13}C = -24^{o}/oo$ to $-34^{o}/oo$), aquatic plants, desert and salt marsh plants, tropical grasses ($\delta^{13}C = -6^{o}/oo$ to $-19^{o}/oo$), algae and lichens ($\delta^{13}C = 12^{o}/oo$ to $-23^{o}/oo$).
2. Concentration and $\delta^{13}C$ value of CO_2 in the environment in which plants incorporate CO_2 (Faure, 1978).
3. Age of organic matter. $\delta^{13}C$ values in general decrease with age due to preferential destruction of organic phases richer in ^{13}C (Faure, 1978).
4. Metamorphism. $\delta^{13}C$ values can become less negative with increasing metamorphic grade because of the formation of methane by thermal cracking of kerogen (Faure, 1978).

A $\delta^{13}C$ value of -26.4 for carbon of the noncarbonate fraction of the Orcas sample points to a biogenic origin. Values for marine sediment have been observed to decrease landward ($-21^{o}/oo$ to $-26^{o}/oo$ for Gulf Coast sediment) and are interpreted as being due to the increased presence of terrestrial plant matter enriched in ^{12}C related to aquatic plants (Sackett and Thompson, 1963). A value of $-26.4^{o}/oo$ might indicate the presence of terrestrial organic matter (derived near shore) for the Orcas sample and might appear to be inconsistent

with a deep marine origin (Vance, 1975). However, values of this order of magnitude are typical of petroleum and natural gas in sedimentary rocks of marine origin.

OXYGEN ISOTOPE COMPOSITION

The $^{18}O/^{16}O$ ratio for the carbonate phase was measured by Geochron Laboratories and reported in standard δ notation relative to Standard Mean Ocean Water (SMOW). The reported value is $\delta^{18}O = +18.9^{o}/oo$.

Factors controlling the $^{18}O/^{16}O$ ratio and hence the $\delta^{18}O$ value for a carbonate include:

1. Temperature of solution (Faure, 1978).
2. The oxygen isotopic composition of H_2O in precipitating solution (Faure, 1978).
3. Fractionation of oxygen isotopes between water and carbonate (Faure, 1978).
4. Age of the sample (Keith and Weber, 1964).

$\delta^{18}O$ (definition relative to SMOW)

$$\delta^{18}O = \frac{^{18}O/^{16}O_{(sample)} - ^{18}O/^{16}O_{(SMOW)}}{^{18}O/^{16}O_{(SMOW)}} \times 10^{3} \text{ ‰}$$

O'Neil and Epstein (1964) determined a fractionation factor of 1.0286 for the calcite - H_2O system at $25^{o}C$ and consequently the reaction: $1/3\ CaCO_3{}^{16} + H_2O^{18} \rightleftharpoons 1/3\ CaCO_3{}^{18} + H_2O^{16}$ leads to about a 2% enrichment in ^{18}O in carbonates precipitated in isotopic equilibrium with H_2O at $25^{o}C$.

Ocean water, at present, has a $\delta^{18}O$ value of about zero. Fresh water is invariably enriched in ^{16}O relative to sea water due to preferential uptake of $H_2{}^{16}O$ during evaporation of seawater and precipitation in a continental environment (Faure, 1978). The $\delta^{18}O$ values for marine carbonates range from

$+28^{o}/oo$ to $+30^{o}/oo$ for recent aged samples to about $+20^{o}/oo$ for old samples (Faure, 1978). The $\delta^{18}O$ values for fresh water carbonates are generally lower and more variable than values for marine carbonates (Faure, 1978).

A $\delta^{18}O$ value $+18.9^{o}/oo$ for the carbonate is within the realm of marine values, however, might be low enough to indicate post depositional exchange with water enriched in ^{16}O. Such changes are expected in rocks which have undergone metamorphism.

SULFUR ISOTOPE COMPOSITION

A homogeneous sample of the pyrite was obtained from the noncarbonate powder. The pyrite's $^{34}S/^{32}S$ ratio was measured by Geochron Laboratories and reported in standard δ notation relative to sulfur in troilite of the iron meteorite Canyon Diablo. The reported value is $\delta^{34}S = +1.5^{o}/oo$.

Factors which control the isotopic composition of sulfides are discussed in Faure, 1978.

This value is typical of sulfides originally from a magmatic source. However, this value does not prove a magmatic origin. Sedimentary sulfides originating from the biogenic reduction of marine sulfate to sulfide by bacteria or sedimentary sulfides having a completely magmatic origin can also possess a $\delta^{34}S$ value of $+1.5^{o}/oo$. The $\delta^{34}S$ values of such sulfides range from $+10^{o}/oo$ to $-50^{o}/oo$ and depend on a complex interaction of environmental factors (H. G. Thode, 1963).

The writer had only one rock sample to work with and any attempt to give a definitive explanation of this value would be premature, for special environmental conditions could be responsible.

STRONTIUM ISOTOPE ANALYSES

Carbonate Minerals

Whole rock powder was prepared from the purest fragments of the rock, i.e., darker fragments indicating a higher proportion of clay minerals were discriminated against. About .25 grams of powder were placed in a clean 50 ml polyethylene beaker. About 25 ml of 0.1 N HCl were used to preferentially dissolve the carbonate phases. The solution was stirred until bubbling ceased and then filtered into a clean 50 ml polyethylene beaker using analytical grade filter paper. 5-10 drops of ^{89}Sr (radioactive tracer) were added to the filtrate and the solution was loaded onto a cation exchange column. (Dowex 50W-x8 organic exchange resin with hydrogen as the exchangable cation). The column was eluted with 2.25 N HCl (prepared as above). Fractions in which ^{89}Sr was detected were combined and evaporated to dryness in a Vycor beaker on a hot plate. Contents of the dish were redissolved with 2.25 N HCl and reloaded onto the exchange column. The column was eluted and 20 15 ml fractions were collected into clean disposable beakers. The radioactivity and Ca concentration of each fraction were determined by a portable Geiger counter and atomic absorption spectroscopy respectively. The results are reported on Fig. 4.

Calcium interferes in the isotope analysis of carbonates. For mass spectrometry it is desirable to choose the collected fractions having the highest measured radioactivities (highest Sr concentrations) provided these fractions have very low calcium concentrations. The graph shows that separation of strontium from calcium during ion exchange was complete. Fractions 15, 16 and 17 were chosen for the final analysis.

The three fractions were combined and evaporated to dryness. Three drops of $HClO_4$ were added to destroy organic exchange resin washed off the column in the elutant. The sample was redissolved with 2 N HNO_3 and evaporated onto the

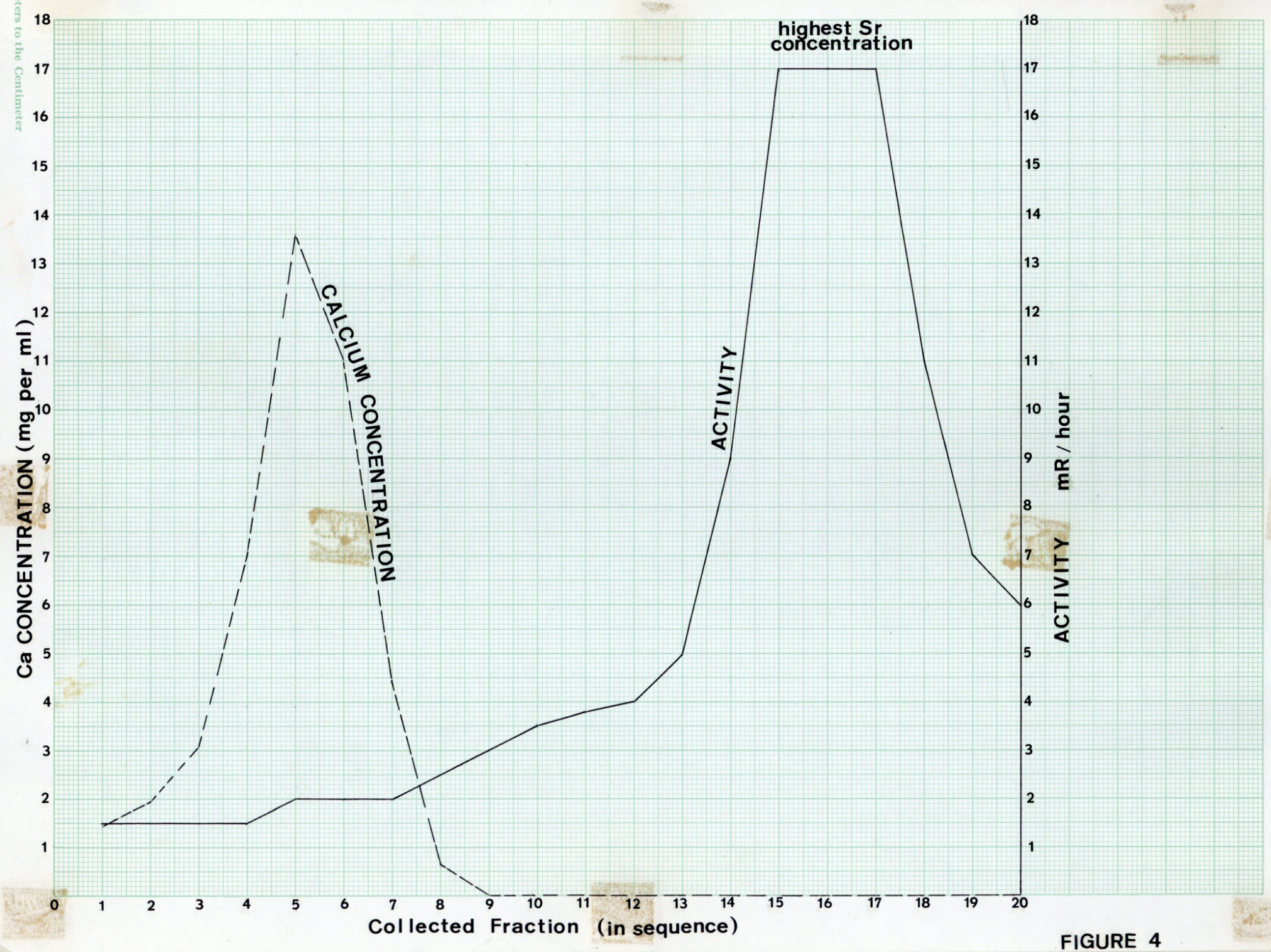

highest Sr concentration
CALCIUM CONCENTRATION
ACTIVITY
Ca CONCENTRATION (mg per ml)
ACTIVITY mR / hour
Collected Fraction (in sequence)
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18

FIGURE 4

clean tantalum filament of the mass spectrometer.

Non-Carbonate Minerals

Approximately 375 g of whole rock powder were placed in a large clean beaker. 2.25 N HCl was added to dissolve carbonate phases; the solution was decanted. The process was repeated twice and pure residue was obtained. The residue was washed three times in double distilled and demineralized H_2O.

The effect of the dissolution of carbonate and washing of the residue on the isotopic composition of strontium within the residue is difficult to ascertain.

The following events could have occurred:

1) Isotopes of strontium released from dissolved carbonate and isotopes of strontium indigenous to the residue were exchanged. Strontium held within the interwater cavity of smectite is easily exchanged. The $^{87}Sr/^{86}Sr$ ratio of the residue could have been altered.
2) Isotope exchange did not occur but perhaps some strontium was leached from the residue in the washing process. The $^{87}Sr/^{86}Sr$ ratio of the residue was not changed by this process.
3) Both 1 and 2 occurred in which case the $^{87}Sr/^{86}Sr$ ratio could have been changed.

The writer will assume that no isotope exchange occurred, but perhaps some strontium, held weakly on clay surfaces, was leached.

1.5 grams of the residue were added to a 5:1 solution of HF and H_2SO_4 (in a polyethylene dish). HF dissolves silicate and H_2SO_4 prevents the precipitation of CaF_2. The dish was covered and heated overnight on a hot plate at 200°C. The solution was evaporated to near dryness the following day. 2.25N HCl and double distilled and demineralized H_2O were added in 1:1 proportions

and then evaporated to a volume of 30 ml. After cooling, the sample was filtered and five drops of ^{89}Sr were added to the filtrate. The remaining procedure is identical to that used for the carbonate.

The Mass Spectrometer

A Nuclide Corporation Model 6-60-S Nier type solid source mass spectrometer (6 inch radius, 60^{o}-sector) was used in the isotope analyses of strontium. The analyses were made at pressure of less than 2×10^{-7} mm Hg.

Peaks were scanned and recorded on a linear strip chart. One scan consists of ^{86}Sr, ^{87}Sr, and ^{88}Sr peaks. The baseline was checked between the ^{87}Sr and ^{86}Sr peaks and adjusted, if necessary. The scanning rate was decreased over the top of the peaks in order to keep the recorder in equilibrium with the detector and obtain flat peaks. Six consecutive scans constitutes one set which was used in the calculation of a $^{87}Sr/^{86}Sr$ ratio and a $^{86}Sr/^{88}Sr$ ratio.

A correction for isotope fractionation during the analysis was made assuming that strontium has an $^{86}Sr/^{88}Sr$ ratio of .1194 and that fractionation of ^{87}Sr relative to ^{88}Sr is ½ that observed for ^{86}Sr relative to ^{88}Sr (Faure, personal communication). The correction factor is $\frac{2\ (86/88)\ \text{Meas.}}{86/88\ \text{Meas.} + .1194}$; corrected values were used to calculate the average set value for an analysis.

The Eimer and Amend Standard was analyzed twice during the period of this investigation. The results are numerically close and compatible with values for Eimer and Amend measured at other laboratories.

TABLE 3 - Results from analyses of Eimer and Amend standard

DATE	87/86 (corrected for fractionation)
2/17/79	0.70799
9/29/78	0.70802

The results obtained in two analyses made on the Orcas carbonate are reported in Table 4.

TABLE 4 - Results from Carbonate Analysis

$^{87}Sr/^{86}Sr$ FIRST ANALYSIS (108 scans)	$^{87}Sr/^{86}Sr$ SECOND ANALYSIS (126 scans)
0.70755	0.70755
0.70865	0.70990
0.70755	0.70561
0.70656	0.70486
0.70971	0.70625
0.70893	0.70862
0.70821	0.70999
0.70569	0.70765
0.70591	0.70882
0.70848	0.71075
0.70776	0.70799
0.70888	0.70739
0.70610	0.70793
0.70663	0.70875
0.70695	0.70648
0.70849	0.70496
0.70856	0.70965
0.71198	0.70618
	0.70921
	0.70869
	0.70389
SAMPLE MEAN $\pm$ $\bar{S}$	SAMPLE MEAN $\pm$ $\bar{S}$

SAMPLE MEAN $\pm$ $\bar{S}$ Combined Analyses (234 scans)

0.70779 ± 0.00028

The chart of the first analysis was read independently by Faure. He calculated an $^{87}Sr/^{86}Sr$ ratio of 0.70782 ± 0.00042 ($\bar{S}$).

The isotope analysis of the noncarbonate consisted of 72 scans. The results, corrected for fractionation, are reported in Table 5.

TABLE 5 - Results from Non-carbonate Analysis

$^{87}Sr/^{86}Sr$
.71353
.71327
.71127
.71056
.71443
.71168
.70950
.70960
.71175
.71278
.71120
.71848

SAMPLE MEAN $\pm$ $\bar{S}$

0.71233 ± 0.00074

THE AGE OF THE CARBONATE

The following calculation shows that post depositional Sr exchange reactions between carbonate and non-carbonate phases and leaching of Sr from the non-carbonate fraction during analysis preparation had an insignificant effect on the $^{87}Sr/^{86}Sr$ ratio for the carbonate phase. The writer will assume a noncarbonate weight percentage, non-carbonate $^{87}Sr/^{86}Sr$ ratio and non-carbonate Sr concentration far exceeding the analytical uncertainty of the measured results: 87/86 = 0.73, Weight % - 5%, Sr con. = 50 mg/g. Now assume complete mixing of non-carbonate strontium with carbonate strontium and note the resulting $^{87}Sr/^{86}Sr$ ratio for the mixture.

$$^{87}Sr/^{86}Sr = \frac{(Srcarb)\ (Ab^{87}carb)(Wnoncarb)f + (Srnoncarb)\ (Ab^{87}noncarb)(Wcarb)(1-F)}{(Srcarb)\ (Ab^{86}carb)(Wnoncarb)f + (Srnoncarb)\ (Ab^{86}noncarb)(Wcarb)(1-F)}$$

MIXTURE AFTER FAURE (1978

W - the atomic weight of strontium
Sr - strontium concentration
f - carbonate weight percentage
Ab^{87} - isotopic abundance of ^{87}Sr
Ab^{86} - isotopic abundance of ^{86}Sr

$$^{87}Sr/^{86}Sr = \frac{(614)(.0698)(87.6146)(.95) + (50)(.0718)(87.608)(.05)}{(614)(.0986)(87.61457)(.95) + (50)(.0984)(87.608)(.05)}$$

$$= 0.708 \approx 0.70779$$

The absolute error is within the analytical uncertainty of the measured value 0.70779 ± 0.00028. The relative error is less than 0.03%.

The writer found no evidence suggesting that the primary ratio was changed subsequent to the carbonates formation and therefore, concludes that 0.70779 was the ratio for sea water at the time of formation.

The result has been plotted on Fig. 5 (Peterman's Graph) allowing for an average standard deviation from the measured value. Choices of possible dates were made by considering all data points falling in the range 0.70751 - 0.70807. These points are shown in red. Consideration was also given to outside points having 95% confidence level bars passing through the value 0.70779. These points are shown in blue. Peterman's data points were connected with line segments assuming a near linear change from one value to the next.

The fields shown in green were taken as the best time resolutions obtainable from both Peterman's and the writer's data. The possible dates are:

1. Early to Middle Tertiary
2. Early to Middle Triassic
3. Late Pennsylvanian
4. Mississippian
5. Late Devonian
6. Early Devonian?
7. Silurian?

The Tertiary date can be disqualified because it post-dates well documented mid-Cretaceous metamorphism. The Triassic age is in agreement with paleontological data and an early Mesozoic age assigned by Vance to the Orcas Formation (see Appendix). Lack of information prevents the disqualification of dates listed above from 3 to 6. A Silurian age can probably be discounted because it would be the oldest age ever reported for a limestone from the area.

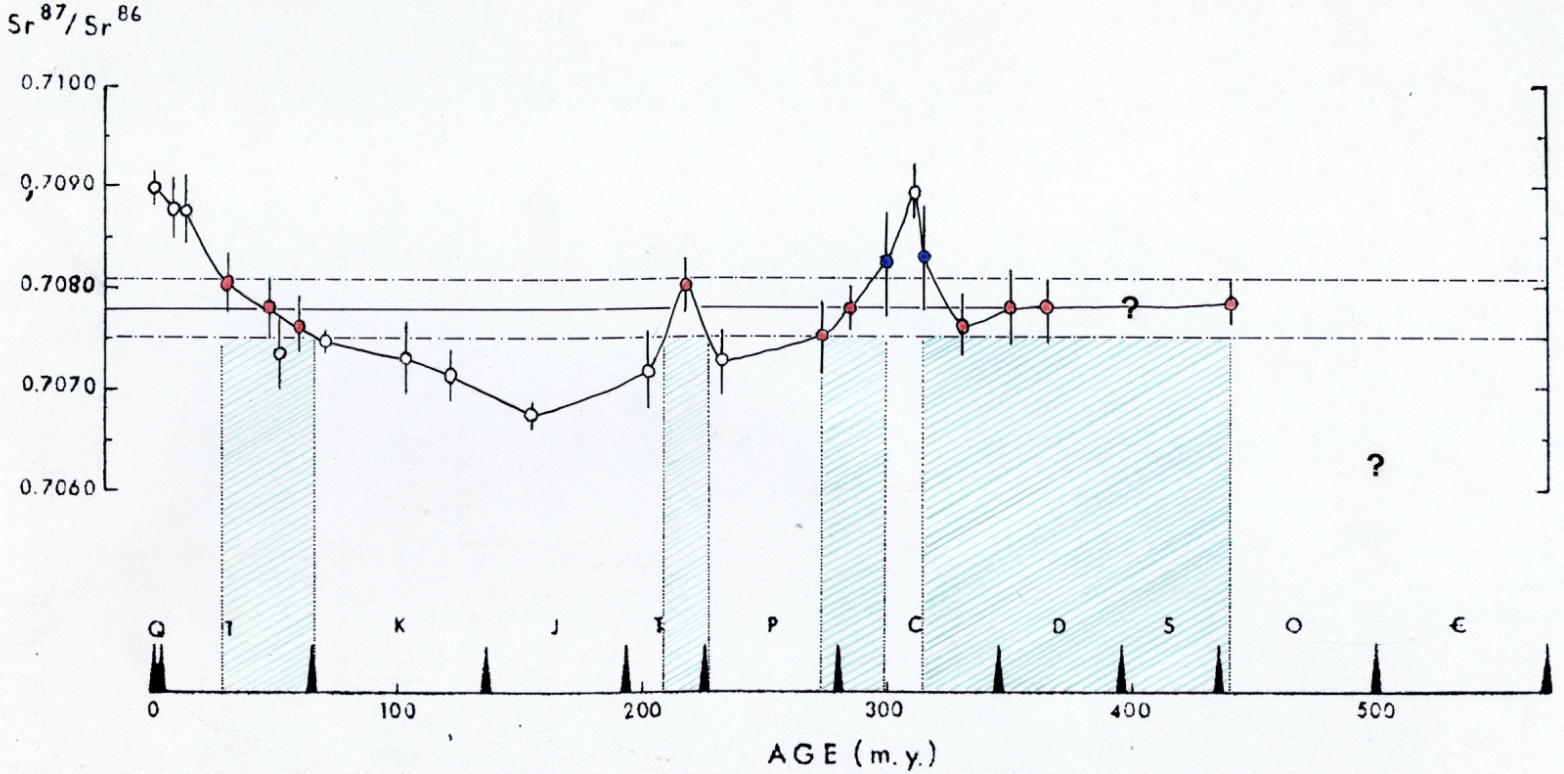


Fig. 2. Variation in Sr^{87}/Sr^{86} values for sea water during most of Phanerozoic time. The vertical bars represent the 95 per cent confidence level about the mean points.

FIGURE 5

INTERPRETATION OF ISOTOPIC COMPOSITION OF SR IN NON-CARBONATE FRACTION

The crystal structures of quartz and pyrite do not favor the substitution of larger cations like Rb(r = 1.48A) and Sr(r = 1.13A). Substitution in quartz is further limited by the markedly different valences of the relevant cations (Si = +4, Rb = +1, Sr = +2). Therefore, the mineral composition of the non-carbonate fraction (clay minerals + quartz + pyrite) allows us to interpret its $^{87}Sr/^{86}Sr$ ratio and Sr and Rb concentrations solely in terms of the clay mineral fraction, the dominant component being a regularly mixed smectite - chlorite clay.

The equation $(^{87}Sr/^{86}Sr) = (^{87}Sr/^{86}Sr)_o + {}^{87}Rb/^{86}Sr\ (e^{\lambda t} - 1)$ whose complete derivation can be found in Faure (1978) is the fundamental equation from which age determinations are made by the Rubidium-Strontium method. The validity of a mineral date obtained from the equation generally depends on the following requirements:

1. The $^{87}Sr/^{86}Sr$ ratio of the mineral changed only as a result of the decay of ^{87}Rb. Rb and Sr were "not added to or lost from the mineral during its lifetime". (Faure, 1978).
2. The minerals present $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ ratios are accurately determined.
3. The initial $^{87}Sr/^{86}Sr$ ratio is known. This may require an assumption. (Faure, 1978).

Figure 6 was constructed in order to determine an age for the clay fraction and to investigate the relationship between the clay fraction and enclosing carbonate phase.

The equation for the solid and dashed diagonal lines labeled "clay mineral fraction" is:

$$\left(\frac{^{87}Sr}{^{86}Sr}\right)_0 = \left(\frac{^{87}Sr}{^{86}Sr}\right) - \left(\frac{^{87}Rb}{^{86}Sr}\right)(e^{\lambda t} - 1)$$

relating the age of the clay fraction to the only unknown parameter $(^{87}Sr/^{86}Sr)_0$ (the initial ratio).

λ is the decay constant for ^{87}Rb ($1.42 \times 10^{-11} y^{-1}$), t is the time elapsed since the mineral (clay fraction) became a closed system with respect to strontium, and $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ are isotopic ratios measured and calculated in the analysis.

The other parameters were determined in the analysis and are:

$\frac{^{87}Sr}{^{86}Sr}$ = Solid diagonal line (0.7123)
Upper dashed line ($0.7123 + \bar{S}$)
Lower dashed line ($0.7123 - \bar{S}$)

^{87}Rb = 1.0853 Calculated from:

$$\frac{\text{Rb conc}}{\text{Sr conc}} \times \frac{\text{Abundance } ^{87}Rb}{\text{Abundance } ^{86}Sr} \times \frac{\text{Atomic weight Sr}}{\text{Atomic weight Rb}}$$

$$= \frac{15}{40} \times \frac{.278346}{.0986} \times \frac{87.6182}{85.46776}$$

No error was allowed for in the value $\frac{\text{Rb conc}}{\text{Sr conc}}$. For low Rb/Sr ratios, the relative error could be large.

The linearity results from the fact that λ is very small and consequently the second derivative:

$$\frac{d^2(^{87}Sr/^{86}Sr)}{dt^2} = -\frac{^{87}Rb}{^{86}Sr}\lambda^2 e^{\lambda t} \approx 0$$

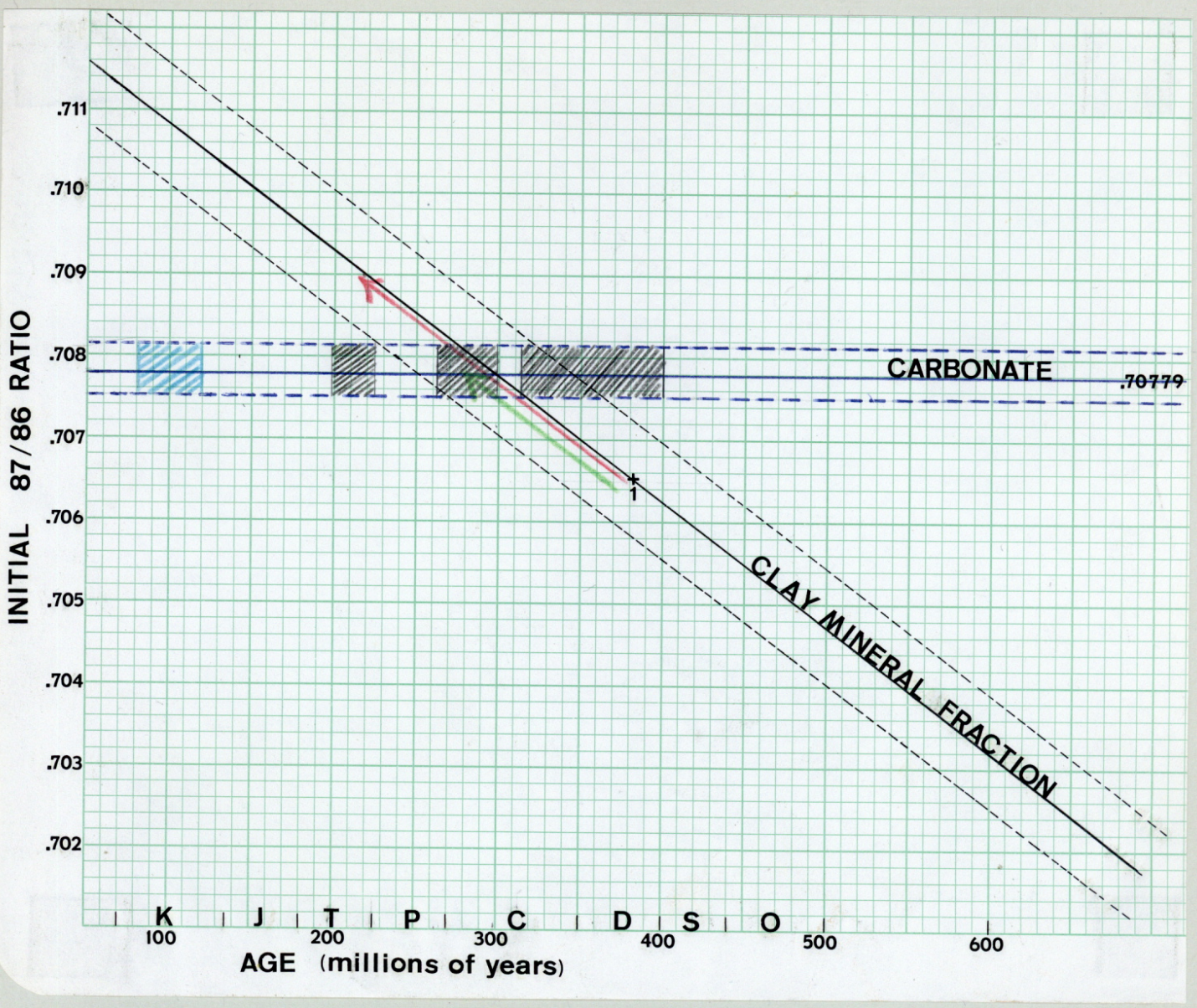

INITIAL 87/86 RATIO
.711
.710
.709
.708
.707
.706
.705
.704
.703
.702
CARBONATE
.70779
1
CLAY MINERAL FRACTION
K
J
T
P
C
D
S
O
100
200
300
400
500
600
AGE (millions of years)

FIGURE 6

The result obtained in the isotope analysis of the carbonate, .70779 $\pm \bar{S}$ ($\bar{S}$ = .00028) was plotted (labeled carbonate). The black shaded areas are the possible carbonate dates.

A number of interpretations are indicated by the graph. First, it appears that equilibration of strontium isotopes between clay mineral and carbonate fractions may not have occurred during the mid-Cretaceous metamorphism. If homogenization had occurred, the $^{87}Sr/^{86}Sr$ ratio for the clay mineral fraction would have closely approached the $^{87}Sr/^{86}Sr$ ratio for the enclosing carbonate (0.70779) during mid-Cretaceous time and would be indicated by the intersection of the diagonal clay mineral field with the horizontal carbonate field in the area shaded in blue. That homogenization may not have occurred is somewhat remarkable in the light of Mid-Cretaceous metamorphic conditions (200-300^{o}C, 2.5-3kB), high ion exchange capacity of smectites, the relative size of the clay mineral "system" with respect to the enclosing carbonate "system" and the probable high flux of strontium the clay mineral system was exposed to during the recrystallization of the carbonate minerals. Clauer (1978) points out that homogenization of sedimentary clay fractions can occur at a temperature of about 250^{o}C and a pressure of about 1kB.

Mid-Cretaceous temperatures and pressures were the highest realized by the rock and if homogenization did not take place then, it is fair to assume it did not occur earlier in the rock's life. Clauer's investigation of smectites from the South Pacific shows that this mineral is "generated" with a $^{87}Sr/^{86}Sr$ ratio equal to 0.7065, intermediate between their parent basalts (0.704 $\pm$ 0.002, Faure and Powell, 1972) and sea water. This has been plotted for the Orcas clay fraction and is labeled (1). The indicated age for the clay is Devonian. The age is valid provided the initial ratio was 0.7065 and the clay remained a closed system during subsequent time.

If these assumptions are true, the clay fraction could have originated from the weathering of rocks making up the Turtleback complex. The Turtleback complex consists of middle Devonian intrusive igneous rocks and associated volcanic rocks (Brown, 1975; Danner, 1977).

These rocks are thought to be the basement rocks of the San Juan Islands (Vance, 1977).

If a Triassic age is accepted for the carbonate phase, a Devonian age for the clay fraction implies residence for 165 my in environments outside of the ocean. It is possible for clay minerals, once formed to remain stable for long periods of time (Keller, 1956) and evidently the initial $^{87}Sr/^{86}Sr$ is not appreciably changed during subsequent weathering (Dasch, 1969). The red arrow illustrates subsequent strontium evolution during the 165 my prior to its introduction into the Triassic carbonate.

Other interpretations of graph 7 are also possible.

1. The carbonate is late Pennsylvanian in age in which case the concordance of the $^{86}Sr/^{87}Sr$ ratios for the carbonate and clay fractions during this time is either:

   a) A coincidence of Sr evolution within the clay (shown with a green arrow - assuming an initial ratio = .7065). This model assumes closed system behavior during the life of the clay.

   b) A consequence of equilibration with the enclosing carbonate due to burial and diagenesis. This model does not assume any initial ratio for the clay fraction. It only assumes closed system behavior after Pennsylvanian. The actual age of the clay could be coeval with or predate the carbonate.

   c) The formation of the clay in complete isotopic equilibrium with late Pennsylvanian sea water as can occur with phillipsite (Clauer, 1978) or equilibration of the clay fraction with sea water just prior to its introduction into the carbonate. Closed system behavior after introduction is assumed.

2. The carbonate is Devonian in age in which case the clay fraction is coeval with the enclosing carbonate. (Assuming initial ratio = .7065 and closed system behavior during the life of the clay).

APPENDIX

Vance has tentatively assigned an early Mesozoic age to the Orcas sediments. This is consistent with Micro and Macro fossil evidence obtained by various investigators. See Map 2. Orcas Island is outlined in red. Indicated on the map are the locations (numbered with arrows) of some of these paleontological finds within the Orcas Cherts on San Juan Island. The numbers are to be correlated with the underlying table listing the investigator, type of fossils found and age assigned.

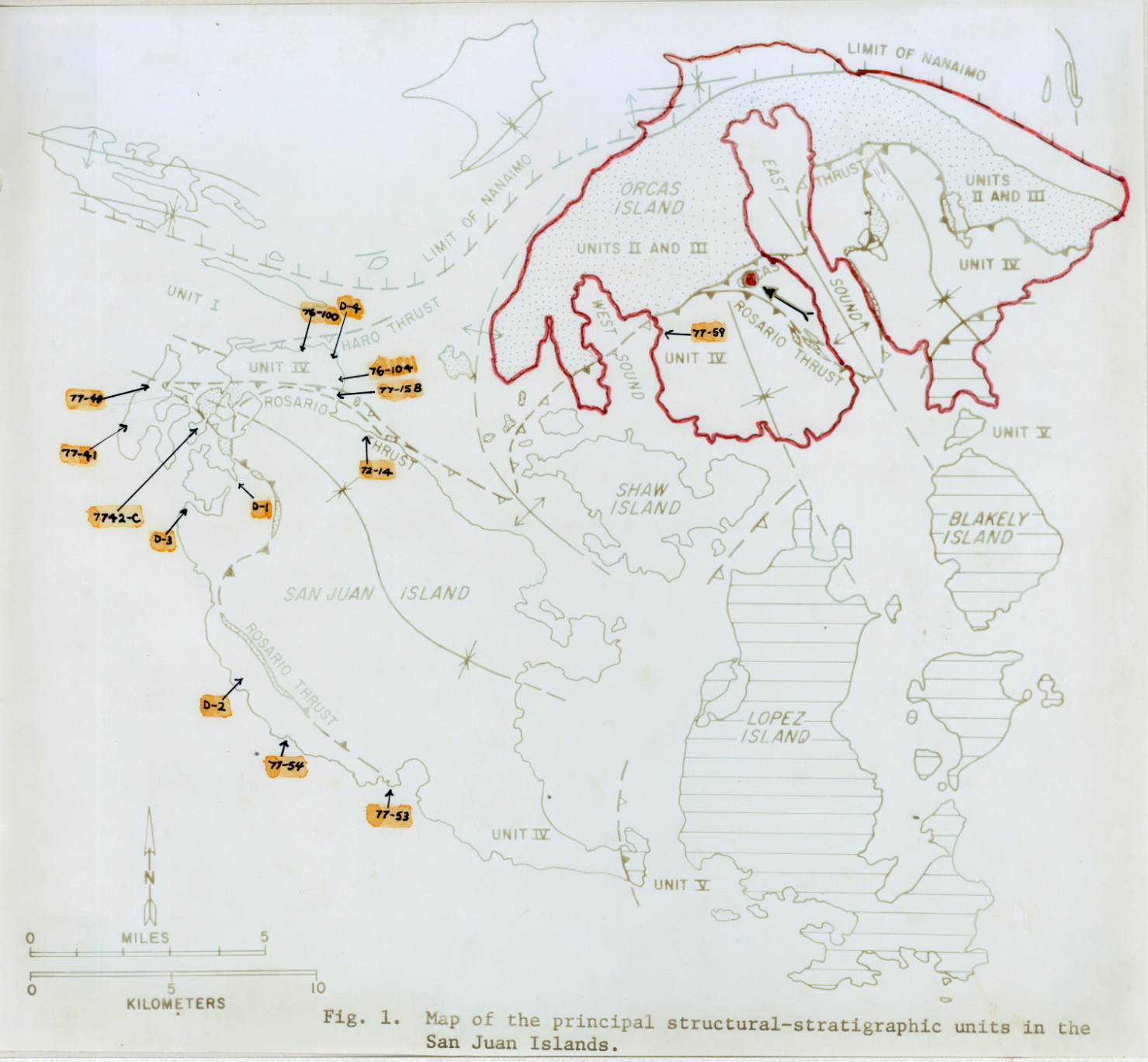


Fig. 1. Map of the principal structural-stratigraphic units in the San Juan Islands.

TABLE 6 (Ages assigned to the Orcas)

Information taken from Whetten et al. (1978)

NUMBER	INVESTIGATOR	FOSSIL TYPES	AGE
D-1	Danner (1966)	Fusilinids	Permian
D-2	Danner (1966)	Fusilinids	Permian
D-3	Danner (1966)	Fusilinids	Permian
D-4	Danner (1966)	Foraminifers	Permian
77-54	D. L. Jones	Radiolarians	Triassic
77-53	D. L. Jones	Radiolarians	Triassic
77-42C	D. L. Jones	Radiolarians	Triassic
77-41	D. L. Jones	Radiolarians	L. Triassic-E. Jurassic
77-40	D. L. Jones	Radiolarians	Triassic
77-14	D. L. Jones	Radiolarians	Triassic
77-59	D. L. Jones	Radiolarians	L. Triassic-E. Jurassic
77-15B	D. L. Jones	Radiolarians	L. Triassic-E. Jurassic
76-100	E. A. Pessagno	Radiolarians	E. Jurassic?
76-104	E. A. Pessagno	Radiolarians	M. -L. Triassic

SUMMARY

A sample of aragonite marble from the Orcas Formation at the McGraw-Kittinger Quarry on Orcas Island, Washington is composed of $\pm$20% aragonite, $\pm$80% calcite and $\pm$4% acid insoluble residue. The residue fraction consists of about $\pm$10% quartz, $\pm$2% pyrite and $\pm$90% clay minerals and is distributed in layered fashion through the rock sample. These layers are probably primary bedding. The dominant clay mineral in the residue fraction is a regularly mixed smectite-chlorite clay and could have formed from original smectite.

The concentration of strontium in the carbonate phase of the rock sample is 614 ppm. This is consistent with the conclusion made by Vance on the basis of mineral associations and structural relations, that the aragonite is a recrystallized metastable product at moderate pressure of original calcite.

The $\delta^{18}O$ and $\delta^{13}C$ values for the carbonate phase of the sample are $\pm$18.9°/oo and $^{+}$3.1°/oo respectively. These values are compatible with a marine origin. The $\delta^{13}C$ value for amorphous carbon in the residue fraction is -26.1°/oo. This value may indicate a photosynthetic origin for carbon in the residue fraction.

The $^{87}Sr/^{86}Sr$ ratio of the carbonate phase is 0.70779 $\pm$ .00028. There is no evidence indicating that the $^{87}Sr/^{86}Sr$ ratio of the carbonate was changed after its formation. This value is therefore taken as the value for sea-water at the time of the carbonate's formation. On the basis of data reported by Peterman et al. (1970) and by geologic relations, the possible ages of precipitation for the carbonate are Early to Middle Triassic, Late Pennsylvanian, Mississippian, Early Devonian, or Late Devonian. The Early to Middle Triassic age is in agreement with paleontological data and an Early Mesozoic age assigned By Vance to the Orcas Formation.

The $^{87}Sr/^{86}Sr$ ratio of the residue fraction is 0.71233 ± 0.00074. Since the only Sr bearing mineral phases of the residue fraction are clay minerals, this value is interpreted solely in terms of the clay mineral fraction. It appears that Sr homogenization between the carbonate and clay mineral fractions of the whole rock did not occur under metamorphic conditions transitional between prehnite-pumpellyite and lawsonite-albite facies during mid-Cretaceous time.

This allows the calculation of a Devonian age for the clay mineral fraction, provided that an initial $^{87}Sr/^{86}Sr$ ratio of 0.7065 is assumed for the clay. The clay fraction could have originated from the weathering of rocks making up the Turtleback complex, consisting of middle Devonian intrusive igneous rocks and associated volcanic rocks and thought to be the basement rocks of the San Juan Islands.

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